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|---|----|-----------|---|
| (51) International Patent Classification 5 : B01J 29/06, 29/28, C07C 51/285 | | A1 | (11) International Publication Number: WO 94/02245 (43) International Publication Date: 3 February 1994 (03.02.94) |
| (21) International Application Number: PCT/EP93/01972 | | | (74) Agents: BAWDEN, Peter, Charles et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB). |
| (22) International Filing Date: 23 July 1993 (23.07.93) | | | (81) Designated States: AU, BR, BY, CA, CZ, JP, KR, PL, RU, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). |
| (30) Priority data: 9215822.9 24 July 1992 (24.07.92) 9307910.1 16 April 1993 (16.04.93) | GB | GB | Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
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(54) Title: CATALYSTS AND THEIR USE IN OXIDATION OF SATURED HYDROCARBONS

(57) Abstract

New titanium zeolite Beta catalysts which have been found to be useful as catalysts for the oxidation of organic compounds using organic hydroperoxides as oxidation catalysts. They are particularly useful as ring opening oxidation catalysts and may be used to produce adipic acid from cyclohexane.

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Catalysts and their use in Oxidation of Saturated Hydrocarbons

The present invention relates to catalyst systems and their use for the oxidation of organic compounds and in particular to the selective oxidation of organic compounds particularly aliphatic compounds and alkyl aromatic compounds. A particularly useful feature is their performance as ring opening catalysts. In a preferred embodiment the invention is concerned with the oxidation of saturated hydrocarbon chains.

Saturated organic compounds are difficult to oxidise and despite attempts to develop methods and techniques for their controlled or selective oxidation techniques using mild conditions with relatively high yields are only known for the conversion of butane via butenes into maleic anhydride, furthermore the known processes use homogenous and sometimes hazardous catalysts requiring complex separation techniques. An example of such processes are given in Catalysis Today Vol. 1 Nos. 5 of October 1987 relative to the selective catalytic oxidation of butane to maleic anhydride involving dehydrogenation and oxidation of the resulting intermediate olefin, the article in Tetrahedron Vol. 31 pages 777-784 concerning the oxidation of cyclohexane with molecular oxygen and the article in the Journal of the CHEM. SOC. CHEM. COMMUN. 1987 page 1487 and Journal of Molecular Catalysis 44 (1988) pages 73-83. The direct oxidation of saturates to introduce functional groups such as ketones and alcohols using a heterogeneous catalyst system would be extremely attractive.

PCT patent application number GB 8901328 describes the use of catalysts based on crystalline synthetic material comprising silicon and titanium oxides and are characterised by an infra red absorption band at around 950 cm^{-1} to 960 cm^{-1} and typically of the general formula:

$$x\text{TiO}_2(1-x)\text{SiO}_2$$

where x is from 0.0001 to 0.04 for the oxidation of saturated hydrocarbons.

These catalysts known as TS-1 and TS-2 are typically prepared in the absence of aluminium from a mixture containing a source of silicon oxide, a source of titanium oxide, a nitrogenated organic base and water as described in United Kingdom Patent 2071071 which is concerned with the catalysts themselves or by

the dealumination of ZSM-5 and reaction with titanium tetrachloride vapour as described by B. Kraushaar and J.H.C. Van Hoof in *Catalysis Letters* 1 (1988) pages 81-84. The catalysts may contain small amounts of other metals such as aluminium, gallium and iron (as described in European Patent Application 5 0226258).

More recently aluminium containing titanium silicalites have been reported for example in EP 0293950 and in *Zeolites* 12 (1992) 135-137. In this case, the catalysts exhibit both oxidising and acidic catalytic activities.

10 In EP 0230949 the treatment of TS-1 catalyst with neutralising agents (e.g. alkaline compounds is reported). The examples given in the patent show that TS-1 catalyst treated with alkaline compounds give better yields of epoxides and lower amounts of by-products when they are used as catalysts for the epoxidation 15 of olefins by H₂O₂. It is suggested that the applied treatments have a neutralising effect on the catalyst's acidity, and thus prevent the catalyst to initiate undesirable side reactions.

Both TS-1 and TS-2 catalysts contain pores with a diameter of \pm 5.5 Å. This 20 limits their application to reactions of relatively small substrates, which can easily enter these pores. For example, in paraffin oxidation, n-hexane is oxidized more easily than cyclohexane, and the reactivity of different paraffins decreases with increasing carbon-number and increasing branching. In order to have suitable 25 catalysts for the oxidation of larger organic substrates, the synthesis of larger pore titanium containing zeolites is highly desirable.

Recently, the synthesis of a titanium containing zeolite isomorphous to zeolite Beta has been reported (*J. Chem. Soc. Chem. Comm.* 1992 (8) 589-590). In the described synthesis method low concentrations of aluminium (Si/Al = 192) are 30 used for the preparation of the synthesis mixture. Like TS-1 and TS-2, the titanium containing zeolite Beta is characterised by an IR absorption at \pm 960 cm⁻¹. It is further reported to catalyse the oxidation with H₂O₂ of cyclohexane to cyclohexanol and cyclohexanone and the oxidation of cyclododecane to cyclododecanol, cyclododecanone, cyclododecene and 35 cyclododecadiols. In these reactions the titanium containing zeolite Beta, which has a pore diameter of 7.5 Å, is reported to be more active than the smaller pore TS-1 catalyst.

These catalysts have been reported as oxidation catalysts using aqueous hydrogen peroxide as the oxidising agent. The use of an aqueous system for oxidising organic compounds gives low yields and slow reaction due to the two phase system.

5

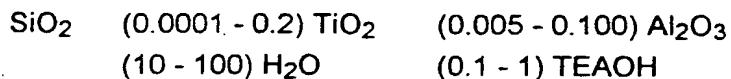
We have now been able to synthesize a titanium containing zeolite Beta in the presence of higher concentrations of aluminium. Addition of aluminium to the synthesis mixture of zeolite Beta is known to increase the efficiency of the synthesis of the zeolite, as described in Zeolites 8 (1988) p 46-53. We have 10 found that the catalysts can be used for oxidation with organic oxidising agents thus enhancing both yield and rate of the oxidation reaction.

15 We have also found that the zeolite Beta obtained is not only a more active catalyst but catalyses other oxidation reactions and has different characteristics from previously reported zeolite Beta.

The new method for the synthesis of titanium containing zeolite Beta consists of the preparation of a synthesis mixture containing a source of titanium (e.g. tetraethylorthotitanate), a source of aluminium (e.g. aluminium powder), a source 20 of silicon (e.g. Ludox AS40, 40% colloidal silica) and an organic N-containing base (e.g. tetraethylammoniumhydroxide (TEAOH)), the ageing of this mixture preferably in the presence of hydrogen peroxide during a predefined period, and the hydrothermal treatment of the mixture. The crystals which are formed during the hydrothermal treatment are then isolated from the mother liquor, washed, 25 dried and finally calcined to remove the organic material contained in the structure.

Typical synthesis mixtures that yield titanium containing zeolite Beta after hydrothermal treatment have the following molar composition

30



It is preferred that the molar ratio of titanium and silicon to that of aluminium in 35 the synthesis mixture is in the range from 10 to 200.

In a preferred process for making the catalyst, hydrogen peroxide is also present. It is preferred to use the amount of hydrogen peroxide which provides from 10 to 200 moles of hydrogen peroxide per mole of tetraethylorthotitanate (TEOT) when that is used as the source of titanium dioxide.

5

The new titanium containing zeolite Beta is highly crystalline and is characterized by an IR absorption at $\pm 960 \text{ cm}^{-1}$ and by an absorption band in Diffuse Reflectance Spectroscopy at the wave number $47,500 \text{ cm}^{-1}$. Diffuse Reflectance Spectroscopy is described in chapter 4 of the book entitled "Characterisation of Heterogeneous Catalysts" by Chemical Industries, Volume 15, published by Manel Dekker Inc. of New York in 1984. The system used was as in Figure 3 of that chapter using a Cory 5 spectrometer.

10 The material has been found to be an active oxidation catalyst especially for reactions involving peroxides as oxidant, particularly organic hydroperoxides not previously used with TS-1 or zeolite Beta. The new catalysts are also effective with hydrogen peroxide oxidation. This oxidative catalytic activity is reminiscent of that reported for TS-1 and TS-2, but compared to those two catalysts titanium containing zeolite Beta is more effective in the oxidation of larger substrates, 20 such as cycloparaffins and cycloolefins. Use of these new catalysts with organic hydroperoxides avoids the two phase system with aqueous hydrogen peroxide and thus increases yield.

25 We have also surprisingly found that when oxidising using hydrogen peroxide the oxidation catalytic performance of titanium containing zeolite Beta irrespective of pore size or aluminium content can be significantly enhanced by treatment of the catalyst with inorganic compounds, preferably acids, bases or ion exchange or by treatment with steam followed by calcination. The treatment is preferably performed before the catalytic reaction is carried out. For example we found that 30 titanium containing zeolite Beta which was treated with a 1.3 N HCl solution and calcined, was more active for the oxidation of cyclohexane by H_2O_2 than the non treated titanium containing zeolite Beta.

Even more surprisingly, we found that the preferred aluminium and titanium 35 containing zeolite Beta of the present invention either treated or not treated, catalyze (ring opening) cyclic compounds to yield acids. For example, the formation of adipic acid was observed in the oxidation of cyclohexane by tertiary

butyl peroxide or H₂O₂ catalyzed by titanium containing zeolite Beta as was the oxidation of cyclopentane to glutaric acid. In this reaction, the catalytic behaviour of titanium containing zeolite Beta is strikingly different from that of TS-1. Under comparable reaction condition using hydrogen peroxide, only cyclohexanols and

5 cyclohexanones are formed on TS-1 whereas high selectivity for adipic acid can be obtained using our new titanium Beta. Selectivity may be further increased particularly with H₂O₂ oxidation if the catalyst has been treated for ion exchange or steam treatment.

10 In the oxidation process of this invention the oxidising agent is hydrogen peroxide or an organic hydroperoxide, examples of suitable organic hydroperoxides include di-isopropyl benzene monohydroperoxide, cumene hydroperoxide, tert.butyl hydroperoxide, cyclohexylhydroperoxide, ethylbenzene hydroperoxide, tert.amyl hydroperoxide, tetriline hydroperoxide and the compound containing

15 the saturated organic group is liquid or in the dense phase at the conditions used for the reaction. It is also preferred that the reaction is carried out in the presence of a suitable solvent. The use of tertiary butyl hydroperoxide is particularly beneficial since the tertiary butyl alcohol produced can readily be converted to the valuable isobutylene molecule.

20 The catalyst used in this invention is preferably prepared from a reaction mixture consisting of sources of silicon oxide, titanium oxide a source of aluminum, a nitrogen containing organic base and water.

25 The silicon oxide source can be a tetraalkylorthosilicate, preferably tetraethylorthosilicate, or simply a silicate in colloidal form.

The titanium oxide source is a hydrolysable titanium compound preferably chosen from TiOCl₄, TiOCl₂ and Ti(alkoxy)₄, preferably Ti(OC₂H₅)₄.

30 The organic base is preferably a tetraalkylammonium hydroxide, and in particular tetraethyl ammonium hydroxide.

In the preferred method to produce the catalyst the mixture of these reactants is

35 subjected to hydrothermal treatment in an autoclave at a temperature of between 130 and 200°C under its own developed pressure, for a time of 1 hour to 30 days preferably 6 to 30 days until the crystals of the catalyst precursor are formed.

These are separated from the mother solution, carefully washed with water and dried.

5 The precursor crystals are then heated for between 1 and 72 hours in air at 200-600, preferably 550°C, preferably during about 20 hours to eliminate the nitrogenated organic base.

10 The catalyst may also contain alkali metal cations M⁺ where M is sodium or potassium and in this situation it is preferred that the molar ratio of M⁺:SiO₂ is in the range 0.001 to 0.5.

It is possible to oxidise saturated aliphatic compounds including aliphatic substituents of aliphatic/aromatic compounds by the process of the invention. The saturated groups which may be oxidised by the process of this invention 15 include long or short, branched or linear alkanes containing 3 or more, preferably 3 to 30, more preferably 3 to 12 carbon atoms, cyclic alkanes and mono- and poly- alkyl aromatics in which at least one of the alkyl groups contain at least two preferably at least three, more preferably 3 to 18, most preferably 3 to 12 carbon atoms and mono- and poly-alkyl cyclic alkanes. The process of the invention is 20 equally applicable to the epoxidation of olefins, dienes, the production of ether glycols, diols, the oxidation of alcohols or ketones, aldehydes, to acids and the hydroxylation of aromatics.

We have surprisingly found that by the selection of appropriate conditions 25 saturated groups may be oxidised with high selectivity to alcohols and ketones under relatively mild conditions. One particularly useful application is in the oxidation of linear and branched paraffins to secondary alcohols and ketones. The process is especially useful in the lower carbon number range to enable use of low-cost propane and butane feedstock in the manufacture of isopropanol 30 alcohol, acetone, secondary butyl alcohol and methyl ethyl ketone. The aliphatic substituent may be a part of a totally aliphatic compound, an aryl compound (alkyl aromatic) or an alkynaphthene compound. Furthermore, said compound may contain other functional groups providing they do not prevent the desired oxidation reaction taking place.

35 The reactivity sequence for the aliphatic compounds slows down from tertiary to secondary and to primary compounds.

The oxidising agents used in the reaction may be organic hydroperoxides, ozone, N₂O or hydrogen peroxide, organic hydroperoxides as described being preferred since the yields and reaction rates are higher than with the aqueous hydrogen peroxide system. When aqueous hydrogen peroxide is used the solution 5 contains from 10-100, preferably 10 to 70 wt% hydrogen peroxide for example diluted hydrogen peroxide (40% by weight in water). It is also preferred that a polar solvent be present when aqueous hydrogen peroxide is used to increase the solubility of the organic compound in the H₂O₂ aqueous phase. Examples of suitable solvents include acetone and methanol.

10

Particular advantages of the present invention are that the process uses mild temperature and pressure conditions and the conversion and yield are high and by-product formation is small. In particular the peroxide conversion is high. The optimum reaction temperature is between 50 and 150°C, preferably about 100°C 15 when using hydrogen peroxide, the temperature may be higher when using organic peroxides, for example up to 200°C. The pressure should be such that all materials are in the liquid or dense phase.

The reaction can be carried out at room temperature but higher reaction rates 20 may be involved at higher temperatures, for example under reflux conditions. Through increase of the pressure either due to the autogeneous pressure created by the heated reactants or by use of a pressurised reactor still higher temperatures can be reached. Use of higher pressures in the range of 1 to 100 bars (10⁵ to 10⁷ Pa) can increase the conversion and selectivity of the reaction.

25

The oxidation reaction can be carried out under batch conditions or in a fixed bed, and the use of the heterogeneous catalyst enables a continuous reaction in a monophase or biphasic system. The catalyst is stable under the reaction conditions, and can be totally recovered and reused.

30

The process of the present invention is preferably carried out in the presence of a solvent. Choice of solvent is important since it should dissolve the organic phase and the aqueous phase when hydrogen peroxide is used which is generally present due to the use of aqueous hydrogen peroxide as the oxidising agent, 35 where organic hydroperoxides are used suitable organic solvents should be used. Polar compounds are preferred which are inert under reaction conditions, and examples of preferred solvents are alcohols, ketones and ethers, with a

number of carbon atoms which is not too high, preferably less than or equal to 6. Methanol or tertiary butanol is the most preferred of the alcohols, acetone and butanone are the most preferred of the ketones. The amount of solvent is important and can influence the reaction product and the conversion, the choice 5 of solvent and the amount depending on the material to be oxidised for example we have found that when oxidising normal hexane with aqueous hydrogen peroxide yields are improved when the ratio of acetone to hexane is in the range 1:1 to 4:1. The solvent improves the miscibility of the hydrocarbon phase and the aqueous phase which is generally present due to the use of aqueous hydrogen 10 peroxide as the oxidising agent. If, however, the peroxide is supplied as a solution, such as tertiary butyl hydroperoxide which is frequently dissolved in ditertiary butyl peroxide, and the substrate is soluble in the solvent then no additional solvent is required.

15 The invention will be described with further details including a preparation of the catalyst and several examples of oxidation reactions.

EXAMPLES

20 **Example 1: Synthesis of Titanium Containing Zeolite Beta**

Six samples of titanium containing zeolite Beta were synthesized from synthesis mixtures with the following molar compositions.

25

Table 1
Molar Compositions of the Synthesis Mixtures

| Sample | TiBeta1 | TiBeta2 | TiBeta3 | TiBeta4 | TiBeta5 | TiBeta6 |
|--------------------------------|---------|---------|---------|---------|---------|---------|
| SiO ₂ | 1 | 1 | 1 | 1 | 1 | 1 |
| TiO ₂ | 0.0286 | 0.0284 | 0.0859 | 0.1718 | 0.0284 | 0.0855 |
| Al ₂ O ₃ | 0.0069 | 0.0074 | 0.0070 | 0.0072 | 0.0200 | 0.0200 |
| TEACH | 0.9576 | 0.9628 | 0.9580 | 0.9580 | 0.9369 | 0.9176 |
| H ₂ O | 79.25 | 80.17 | 80.18 | 80.96 | 78.77 | 77.92 |

Tetraethylorthotitanate (TEOT) was used as a source of TiO₂

Ludox AS40 (40% colloidal silica, Du Pont) was used as a source of SiO₂. Al powder was used as a source of Al₂O₃.

The synthesis mixtures were prepared as follows:

5

The required amount of TEOT was added to water and then cooled to 5°C. To the resulting white suspension, precooled H₂O₂ (35 wt% in water) was added so that a yellow solution was obtained.

10

The following amounts of H₂O₂ were used.

| | TiBeta1 | TiBeta2 | TiBeta3 | TiBeta4 | TiBeta5 | TiBeta6 |
|--|---------|---------|---------|---------|---------|---------|
| H ₂ O ₂ :TEOT Ratio | 95 | 185 | 62 | 31 | 185 | 62 |

15

This solution was kept stirring at 5°C during 3 hours. The required amounts of Al powder and tetraethylammoniumhydroxide (TEAOH) (40% in water) were mixed and heated to 80°C during 3 hours in order to dissolve the Al powder. The water was added and the solution cooled to 5°C.

20

The Ti and Al containing solutions were mixed and kept stirred at 5°C for 1 hour. Then the required amount of Ludox AS40 was added and the mixture kept at room temperature for 18 hours. It was then heated to 70°C for 2 hours and cooled to room temperature again.

25

After addition of some ethanol (\pm 10 ml per 175 ml synthesis mixture), the mixture was transferred to a stainless steel autoclave with a volume of 130 ml. The autoclave was kept at 135°C for 6 days. For the synthesis of TiBeta samples, 1, 2, 3 and 6 the autoclave was static, for the synthesis of TiBeta 4 and 5 the autoclaves were rotated. After 6 days (10 days for sample TiBeta 3), the autoclave was cooled, the solid material contained in it was separated from the mother liquor, washed with water by subsequent centrifugations, and dried at 60°C.

30

Finally the samples were calcined at 550°C in air for 12 hours.

cases. All samples were characterized by an IR absorption band at around $\pm 960 \text{ cm}^{-1}$.

Example 2: Oxidation of n-hexane by H₂O₂

5 TiBeta samples 1, 2 and 5 prepared in Example 1 were used as catalysts for the oxidation of n-hexane by H₂O₂. The catalysts were either used as such or after treatment with inorganic acids, bases or steam. The reactions were carried out at 100°C using the conditions specified in Table 2. The observed n-hexane
10 conversions and product selectivities are listed in Table 2. Acetone was used as solvent except in Experiment 2 which used methanol.

The results show that all samples catalyze the oxidation of n-hexane to 2- and 3-
15 hexanols and hexanones. Comparison of the conversion obtained in experiment No. 3 with that obtained in experiment No. 1 shows that the oxygenation activity of the catalysts in this reaction can be improved significantly by treating them with acids or bases. The high conversion obtained in experiment No. 7 shows that steaming of the catalyst also has a positive effect on their oxygenation activity.

20 Example 3: Oxidation of Cyclohexane by H₂O₂

TiBeta samples 1, 2, 3 and 6 prepared in example 1 were used as catalysts for the oxidation of cyclohexane by H₂O₂. The catalysts were either used as such or after treatment with acids, bases or steam. For comparison, two existing
25 catalysts TS-1 (synthesized according to the procedure described in example 2 of US patent 4,410,501) and TiBeta (synthesized according to the procedure described in J. Chem. Soc. Chem. Comm. 8 (1992), with x = 0.023) (Experiment 9 of Table 3), were also tested as catalysts for the oxidation of cyclohexane, surprisingly Experiment 9 produced a very small amount of adipic acid although
30 this is not reported in the article.

The reaction conditions and the observed cyclohexane conversions and product selectivities are listed in Table 3. 2-Butanone was used as solvent for Experiments 4-9 and acetone was used for Experiments 2 and 3. Experiment 1
35 was solvent free.

Table 2 - Oxidation of n-Hexane

| Exp. No. | Catalyst | Reaction Conditions | | | | | Product Selectivity (%) | | | | | |
|-------------|----------|-------------------------------|---------------------------|--------------------|--|---------------------------|---------------------------|-----------------------------|---------------|---------------|----------------|----------------|
| | | Treatment(s) ^a | Amount Catalyst (g) | n-hexane (mmol) | H ₂ O ₂ ^b (mmol) | Amount Solvent (ml) | Reaction Time (hrs) | Convers. n-hexane (%) | 2- hexanol | 3- hexanol | 2- hexanone | 3- hexanone |
| 1 | TiBeta1 | / | 0.20 | 117 | 234 | 45 ml | 16 | 2.7 | 25 | 23 | 30 | 22 |
| 2 | TiBeta1 | NH ₃ /Na/C | 0.23 | 119 | 226 | 45 ml | 22 | 2.3 | 27 | 27 | 27 | 19 |
| 3 | TiBeta1 | NH ₃ /Na/C/A/ C | 0.07 | 117 | 280 | 45 ml | 22 | 6.9 | 24 | 27 | 25 | 24 |
| 4 | TiBeta2 | A/C | 0.54 | 118 | 234 | 45 ml | 23 | 8.2 | 20 | 16 | 33 | 31 |
| 5 | TiBeta5 | A/C | 0.50 | 113 | 230 | 34 g | 22 | 6.7 | 13 | 11 | 42 | 34 |
| 6 | TiBeta5 | A/C/S/A/C | 0.11 | 113 | 230 | 34 g | 22 | 9.9 | 18 | 15 | 34 | 33 |
| 7 | TiBeta5 | Ss | 0.50 | 113 | 230 | 34 g | 22 | 10.3 | 20 | 16 | 36 | 28 |
| 8 | TiBeta5 | Ss/A/C | 0.50 | 113 | 230 | 34 g | 22 | 9.0 | 14 | 12 | 40 | 34 |

^a: Treatments are carried out subsequently:NH₃: catalyst is put in as an aqueous NH₃ solution of pH 11.8 at room temperature during ½ hour, recovered by centrifugation and washed with distilled water.

Na: catalyst is put in a 0.056 wt% solution of NaCl in water at room temperature during 20 hours, recovered by centrifugation and washed with distilled water.

C: calcination at 550°C under air.

A: catalyst is put in a 1.3 HCl solution at reflux temperature during 3 hours, recovered by centrifugation and washed with distilled water.

S: catalyst is contacted with water until incipient wetness, and heated at 550°C during 1 hour in a covered crucible.

Ss: catalyst is heated at 700°C under N₂ flow and a water flow of ± 50 ml water/g catalyst, hr is brought through the catalyst bed during 1 hour.^b:

Table 3 - Oxidation of Cyclohexane

| Exp. No. | Catalyst | Treatment(s) ^a | Reaction Conditions | | | | | | Product Selectivity (%) | | | | |
|-------------|----------|---------------------------|---------------------------|----------------------------|--|---------------------------|---------------------------|--------------------------|-------------------------|---------------------------|----------------------------|-----------------------------|-----------------------|
| | | | Amount Catalyst (g) | Cyclo- hexane (mmol) | H ₂ O ₂ ^b (mmol) | Amount Solvent (ml) | Reaction Time (hrs) | Reaction Temp (°C) | Cyclo- hexane (%) | Cyclo- hexanol none | Cyclo- hexane- diols | Cyclo- hexane- diones | Adipic Acid (%) |
| 1 | TiBeta1 | NH ₃ /Na/A/C | 0.21 | 136 | 230 | 0 | 1 | 94 | 0 | / | / | / | / |
| 2 | TiBeta2 | NH ₃ /Na/A/C | 0.11 | 143 | 214 | 20 ml | 3 | 94 | 2.5 | 44 | 56 | / | / |
| 3 | TiBeta2 | A/C | 0.34 | 139 | 238 | 45 ml | 22 | 97 | 7.6 | 33 | 67 | / | / |
| 4 | TiBeta2 | A/C | 0.18 | 32 | 94 | 56 g | 4 | 97 | 25.8 | 7.1 | 12.5 | 0.8 | 23.2 |
| 5 | TiBeta3 | / | 0.20 | 33 | 94 | 56 ml | 16 | 97 | 28.0 | 16.9 | 0 | 21.4 | 2.2 |
| 6 | TiBeta3 | NH ₃ /Na/C/A/C | 0.07 | 33 | 94 | 56 ml | 4 | 96 | 47.0 | 0.8 | 4.0 | 12.0 | 4.1 |
| 7 | TiBeta6 | / | 0.20 | 33 | 94 | 56 g | 4 | 100 | 16.7 | 10.8 | 13.9 | 46.7 | 16.3 |
| 8 | TS-1c | / | 0.20 | 33 | 94 | 56 g | 4 | 96 | 16.0 | 20.1 | 8.9 | / | 22.6 |
| 9 | TiBeta | / | 0.20 | 33 | 94 | 56 g | 4 | 97 | 19.0 | 5.4 | 9.1 | 77.4 | 7.0 |

a: Treatments are carried out subsequently:
NH₃: catalyst is put in an aqueous NH₃ solution of pH 11.8 at room temperature during ½ hour, recovered by centrifugation and washed with distilled water.

Na: catalyst is put in a 0.056 w% solution of NaCl in water at room temperature during 20 hours, recovered by centrifugation and washed with distilled water.

c: calcination at 550°C under air.

A: catalyst is put in a 1.3 HCl solution at reflux temperature during 3 hours, recovered by centrifugation and washed with distilled water.

S: catalyst is contacted with water until incipient wetness, and heated at 550°C during 1 hour in a covered crucible.

Ss: catalyst is heated at 700°C under N₂ flow and a water flow of ± 50 ml water/g catalyst, hr is brought through the catalyst bed during 1 hour.

b: A 35% solution of H₂O₂ in water was used.

c: Comparative.

The data illustrates that in the presence of a solvent all catalysts are active for the oxidation of cyclohexane by H₂O₂, with formation of cyclohexanol and cyclohexanone. In acetone, these are the only observed oxidation products in 2-butanone however, cyclohexanediols, cyclohexanedions and adipic acid are 5 also observed upon oxidation of cyclohexane. In experiment No. 6 adipic acid is even the main oxidation product. On the comparative catalyst TS-1 however, no formation of adipic acid occurs under comparable reaction conditions.

Comparison of the cyclohexane conversions obtained in experiments 6 and 7
10 shows again that the oxygenation activity of titanium containing zeolites Beta is greatly improved by treatment of the catalysts with acids or bases.

Example 4

15 The process of the present invention was compared with that described in the Journal Chem. Soc. Chem. Commun. 1992 (8) 589-590 with the following results. This shows that the latter has a lower activity and does not produce adipic acid under identical experimental conditions.

20

Table 4

Oxidation of Cyclohexane with T-BuOOH as the Oxidant in the Presence of Ti β and the Catalyst Synthesised as Described in J. Chem. Soc.

| | Ti β | J. Chem. Soc. |
|--|------------|---------------|
| Reaction Conditions (stirred batch) | | |
| Catalyst (wt%) | 2 | 2 |
| t-BuOOH/Cyclohexane (mol/mol) | 2.4 | 2.4 |
| Solvent | 0 | 0 |
| Time (h) | 4 | 4 |
| Temperature (°C) | 100 | 100 |
| Results - Mole% | | |
| Cyclohexane Conversion | 35 | 16 |
| Selectivity | | |
| Cyclohexanol | 15 | 2 |
| Cyclohexanone | 4 | 2 |
| 1,4-cyclohexanedione | 0 | 27 |
| Adipic Acid | 77 | 0 |
| Others | 4 | 69 |

Example 5

The process of the present invention was used to oxidise 1-octanol.

5

Table 5
Oxidation of 1-Octanol with Ti β and tBuOOH to
the Corresponding Acid: Octanoic Acid

| Reaction Conditions: | |
|---------------------------------------|------|
| Catalyst (wt %) | 2 |
| tBuOOH/1C ₈ OH (mole/mole) | 1:1 |
| Solvent | none |
| Time (h) | 4 |
| Temperature °C | 100 |
| The following was obtained: | |
| Conversion (%) mole | 50 |
| Octanoic Acid (%) mole | 75 |
| Octanal (%) mole | 7 |
| Unknowns (%) mole | 18 |

10 Example 5 of EP 0102655 A2 shows that when using TS-1 as the catalyst and H₂O₂ as the oxidant no octanoic acid is formed.

Example 6

15 The process of the present invention is used to oxidise cyclopentane with hydrogen peroxide and was compared with the yield using TS-1 as catalyst.

Table 6
Oxidation of Cyclopentane with Hydrogen Peroxide
in the Presence of Ti β and TS-1 Respectively

| | Ti β | TS-1 |
|---|------------|------|
| Reaction Conditions (stirred batch): | | |
| Catalyst (wt%) | 6.7 | 6.4 |
| Cyclopentane (mmol) | 40 | 42 |
| H ₂ O ₂ (mmol) | 94 | 96 |
| Acetone (g) | 45 | 45 |
| Reaction time (h) | 24 | 24 |
| Results - mole%: | | |
| Cyclopentane Conversion | 50 | 36 |
| Selectivity: | | |
| Cyclopentanol and Cyclopentanone | 34 | 60 |
| Glutaric Acid | 37 | 8 |
| Others | 29 | 32 |

5

The Diffuse Reflectance Spectroscopy traces for the titanium Beta (a) of the invention and the product synthesis according to the Journal of the Chemical Society (b) are shown in Figure 1 and the Infra Red Spectra are shown in Figure 2.

10

Example 7: Oxidation of Toluene

The process of the present invention was used to oxidise toluene.

Table 7
Oxidation of Toluene in the Presence of Ti- β /t-BuOOH

| Reaction Conditions: | |
|-----------------------------|------|
| Catalyst (wt%) | 0.73 |
| t-BuOOH/toluene (mole/mole) | 1.70 |
| Solvent | none |
| Time (h) | 4 |
| Temperature (°C) | 104 |
| Results - mole%: | |
| Toluene conversion | 25 |
| Selectivity - mole%: | |
| Benzylalcohol | 21 |
| Benzaldehyde | 34 |
| Benzoic acid | 21 |
| Phenol | 6 |
| o-cresol | 0.8 |
| p-cresol | 3 |
| Unknowns | 14.2 |

5 Example 8

Various catalysts were prepared using the conditions set out in Table 7 and their properties were found to be as set out in Table 8.

Table 8

| Synthesis Code | Gel Composition (molar ratios) | | | | Crystallization Conditions | | | | |
|-------------------|--|------------------------------------|---------------------|-----------------------|--|---------------------------|--------------------|--------------|-----------------|
| | SiO ₂ /Al ₂ O ₃ | SiO ₂ /TiO ₂ | OH/SiO ₂ | EtOH/SiO ₂ | H ₂ O/SiO ₂ ^a | Evap. time at 70°C (h) | Head-space (°C) | Temp (°C) | Time (days) |
| 10 | ∞ | 31 | 0.52 | 0 | 12 | 0 | 12 | 125 | 6 |
| 11 | 26 | 31 | 0.52 | 1 | 12 | 0 | 12 | 125 | 6 |
| 12 | 5 | 143 | 0.94 | 2 | 95 | 0 | 40 | 150 | 7 |
| 13 | 5 | 147 | 0.95 | 2 | 98 | 4 | 33 | 125 | 6 |
| 14 | 35 | 145 | 0.96 | 2 | 98 | 2 | 50 | 125 | 6 |
| 15 | 12 | 143 | 0.96 | 2 | 99(42) | 2 | 50 | 135 | 10 |
| 16 | 12 | 50 | 0.96 | 2 | 100(25) | 2 | 50 | 135 | 10 |
| 17 | 18 | 142 | 0.98 | 1 | 40(25) | 2.5 | 5 | 140 | 11 |
| 18 | 18 | 142 | 0.98 | 1 | 40(25) | 2.5 | 5 | 140 | 13 |
| 19 | ∞ | 143 | 0.98 | 1 | 42(28) | 2.5 | 5 | 140 | 11 |
| 20 | 38 | 385 | 0.55 | 0 | 22 | 0 | 50 | 135 | 10 ^b |

a H₂O/SiO₂: Values between brackets indicate the H₂O/SiO₂ ratio after evaporation.

b Agitation is used at 50 rpm.

| Synthesis Code | Remarks | Yield(%) | XRD | IR | | | DRS | | |
|-------------------|--|----------|--------------------------------|----------------------|----------------------|----------------------|----------------------------|----------------------------|----------------------------|
| | | | | 960 cm ⁻¹ | 675 cm ⁻¹ | 525 cm ⁻¹ | 30,800 cm ⁻¹ | 34,000 cm ⁻¹ | 47,500 cm ⁻¹ |
| 10 | NaOH added | 35 | β | no | yes (s) | yes (s) | no | no | no |
| 11 | NaOH added | 35 | Tiβ | no | yes (s) | yes (s) | yes (s) | yes (s) | no |
| 12 | Ludox HS40/H ₂ O ₂ /no aging | 0 | amorphous | no | no | yes (s) | yes (s) | yes (s) | no |
| 13 | Ludox HS40/H ₂ O ₂ /aging | 4 | Tiβ | yes (w) | yes (s) | yes (s) | yes (vw) | yes (w) | yes (s) |
| 14 | Ludox AS40/H ₂ O ₂ /aging | 20 | Tiβ | yes (s) | yes (s) | yes (s) | no | no | yes (s) |
| 15 | more Ti/increased time and temp. | 35 | Tiβ | yes (s) | yes (s) | yes (s) | no | no | yes (s) |
| 16 | more Al | 75 | Tiβ | yes (s) | yes (s) | yes (s) | no | yes (s) | yes (s) |
| 17 | small head-space | 55 | Tiβ | yes (s) | yes (s) | yes (s) | no | no | yes (s) |
| 18 | large head-space/high ethylene pressure | 55 | Tiβ | yes (s) | yes (s) | yes (s) | no | no | yes (s) |
| 19 | no Ti | 42 | β | no | yes (s) | yes (s) | no | no | no |
| 20 | | 10 | J. Chem. Soc. 589 (1992) | yes (vw) | yes (s) | yes (s) | yes (w) | yes (s) | no |

Yield (%): The synthesis yields is defined as weight of calcined zeolite obtained * 100.

weight of SiO₂ + Al₂O₃ in the gel

XRD: Crystalline phase obtained.
 IR: The bands at 575 and 525 cm⁻¹ are typical zeolite Beta framework vibrations; the band at 960 cm⁻¹ is assigned to Ti=O vibrations.
 Indications between bracket (arbitrary): vw = very weak, w = weak and s = strong.
 DRS: The band around 30,800 cm⁻¹ is assigned to agglomerated TiO₂ (e.g. anatase); finely dispersed TiO₂; isolated titanium.

34,000 cm⁻¹

47,500 cm⁻¹

These results again show the difference between the titanium Beta of the invention (11 to 18) with zeolite Beta (10 and 19) and the titanium Beta synthesised according to the Journal of the Society of Chemistry Comm. 8 (1992) (synthesis 20).

Claims:

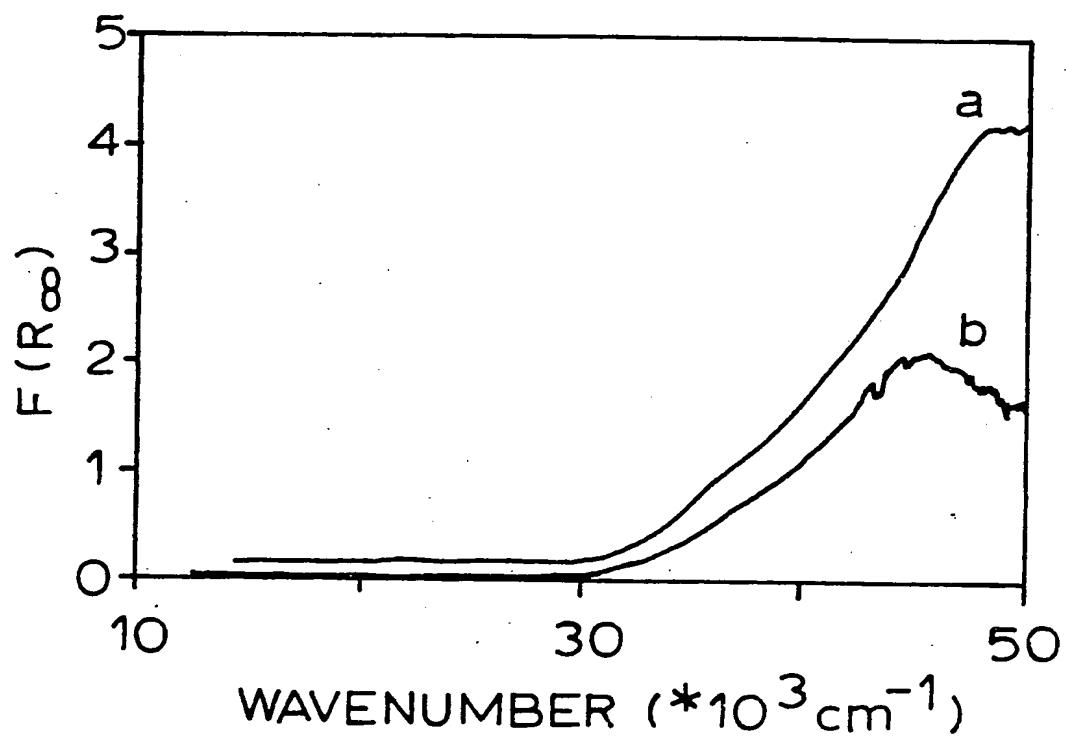
1. The use of titanium containing zeolite Beta as catalyst for the oxidation of organic compounds using organic hydroperoxides and/or N₂O as oxidation catalysts.
2. The use according to claim 1 in which the catalyst is prepared in the presence of hydrogen peroxide from a synthesis mixture that yields titanium containing zeolite Beta after hydrothermal treatment that has the following molar composition

| | | |
|------------------|-------------------------------|--|
| SiO ₂ | (0.0001-0.2) TiO ₂ | (0.005-0.100) Al ₂ O ₃ |
| | (10-100) H ₂ O | (0.1-1) TEAOH |

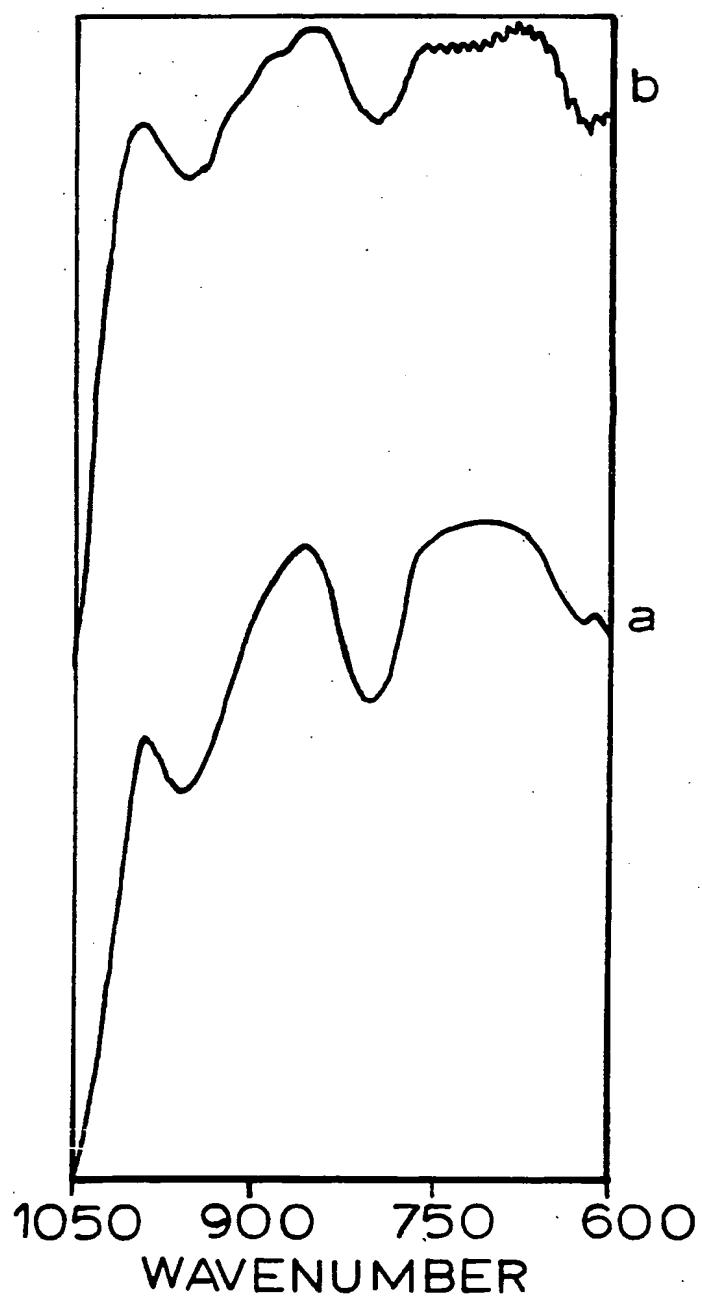
- 15 3. The use according to claim 2 in which the molar ratio of titanium and silicon to that of aluminium in the synthesis mixture is in the range from 10 to 200.
- 20 4. The use according to claim 2 or claim 3 in which the hydrogen peroxide is present in an amount which provides 10 to 200 moles per mole of TEOT when TEOT is used as the source of titanium oxide.
- 25 5. The use according to any of the preceding claims in which the catalyst has been post treated.
6. The use according to claim 5 in which the post treatment is with inorganic acid.
- 30 7. The use according to claim 5 in which the post treatment is with inorganic base.
8. The use according to claim 5 in which the post treatment is with steam.
- 35 9. The use according to any of claims 5 to 8 in which the post treatment is followed by calcination.

10. A titanium containing zeolite beta having an absorption band in Diffuse Reflectance Spectroscopy at the wave number at 47500 cm⁻¹.
11. A process for the production of adipic acid comprising oxidising cyclohexane with a hydroperoxide in the presence of a catalyst according to claim 10.

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FIG. 1

2/2

FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 93/01972

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: B01J 29/06, B01J 29/28, C07C 51/285
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: B01J, C01B, C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
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| X | US, A, 4490565 (CLARENCE D. CHANG ET AL), 25 December 1984 (25.12.84), column 2, line 63; column 3, line 28; column 3, line 55 - line 59, column 4, line 14 -- | 1,5,8 |

 Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search

27 October 1993

Date of mailing of the international search report

01.12.93

Name and mailing address of the International Searching Authority



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INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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INTERNATIONAL SEARCH REPORT
Information on patent family members

01/10/93

International Application No.

PCT/EP 93/01972

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
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